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(54) Polarizable electrode for double-layer capacitor and process of manufacturing thereof.

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(57) The present invention provides; (1) a polarizable electrode for electric double-layer capacitor, which comprises a solid active carbon obtained by pyrolyzing a mixture mainly containing an active carbon and a thermosetting resin and which has, on the surface and/or inside, discontinuous portions free from said solid active carbon; (2) a process for producing the above polarizable electrode for electric double-layer capacitor, which comprises heat-treating, as necessary, a mixture mainly containing an active carbon, a thermosetting resin and a fiber capable of vaporizing upon heating, to vaporize said fiber and then pyrolyzing the resulting material; and (3) an electric double-layer capacitor comprising at least a pair of the above polarizable electrode for electric double-layer capacitor and an electrolyte impregnated between said polarizable electrodes.

The above polarizable electrode for electric double-layer capacitor is free from the drawbacks of conventional polarizable electrodes, has a low internal resistance and can be charged with or can discharge a large electric current of several amperes to several hundreds of amperes momentarily.

## Background of the Invention

## (1) Field of the Invention

5 The present invention relates to a polarizable electrode for electric double-layer capacitor, a process for producing said polarizable electrode, and an electric double-layer capacitor using said polarizable electrode.

## (2) Description of the Prior Art

10 Electric double-layer capacitors are in use in the form of a small but large capacitance capacitor as a backup electric source for memory of microcomputer, etc. Electric double-layer capacitors commercialized currently, however, have a high internal resistance and allows for charging and discharging of only up to about several milliamperes. Hence, it is desired to develop an electric double-layer capacitor capable of being charged with or discharging a large electric current of several amperes to several hundreds of 15 amperes momentarily.

With respect to the polarizable electrode for use in electric double-layer capacitor, capable of being charged with or discharging a large electric current, there have hitherto been made various proposals. There were proposed, for example, a paste-like polarizable electrode obtained by mixing an active carbon powder and an electrolyte [Japanese Patent Application Kokai (Laid-Open) No. 102914/1989] and a 20 polarizable electrode using an active carbon fiber [Japanese Patent Application Kokai ( Laid-Open) No. 141629/1991]. These polarizable electrodes using an active carbon powder or an active carbon fiber, however, have a high internal resistance owing to the weak contact between active carbon particles, or cause reduction in capacity owing to the falling off of powder or detachment of fiber.

Hence, there was proposed a polarizable electrode obtained by pyrolyzing a mixture of an active 25 carbon powder and a phenol in an inert atmosphere [Japanese Patent Application Kokai (Laid-Open) No. 288361/1992.] In this polarizable electrode, however, an electrolyte is unable to infiltrate sufficiently into the electrode when the electrode is thick and, as a result, the capacitor assembled with the electrode has an increased internal resistance. There was also proposed an activated porous carbon material obtained by 30 pyrolyzing a phenol foam having cells perpendicular to the electrode surface and then activating the resulting material [Japanese Patent Application Kokai (Laid-Open) No. 177713/1992]. In this polarizable electrode obtained by activating a carbon foam of block form, there are no increase in internal resistance and the falling-off of powder; however, the activation remains only at the surface and it is impossible to make the large electrostatic capacity per unit volume or unit weight.

Further, a very small amount of the alkali metal or alkaline earth metal contained in the foam as a 35 foaming agent, when the electrode is assembled into a capacitor, shortens the cycle life of the capacitor.

## Object and Summary of the Invention

The object of the present invention is to provide a polarizable electrode for electric double-layer 40 capacitor, which is free from the above-mentioned drawbacks of the prior art and which has a low internal resistance and can be charged with or discharge a large electric current of several amperes to several hundreds of amperes momentarily; a process for producing such a polarizable electrode; and an electric double-layer capacitor using such a polarizable electrode.

In the course of a study to achieve the above objects, the present inventors thought of an idea that a 45 polarizable electrode having discontinuous portions (e.g. throughholes) on the surface and/or inside can easily be impregnated with an electrolyte and enables easy migration of the ion in said electrode and, as a result, such an electrode has a low internal resistance even though it has a large thickness and need not contain any foaming agent (e.g. alkali metal or alkaline earth metal), whereby an electric double-layer capacitor having a long cycle life may be provided. The present inventors made a further study based on 50 the idea and completed the present invention.

The present invention provides:

a polarizable electrode for electric double-layer capacitor, which comprises a solid active carbon obtained by pyrolyzing a mixture mainly containing an active carbon and a thermosetting resin and which has, on the surface and/or inside, discontinuous portions free from said solid active carbon,

55 a process for producing the above polarizable electrode for electric double-layer capacitor, which comprises heat-treating, as necessary, a mixture mainly containing an active carbon, a thermosetting resin and a fiber capable of vaporizing upon heating, to vaporize said fiber and then pyrolyzing the resulting material, and

an electric double-layer capacitor comprising at least a pair of the above polarizable electrode and an electrolyte impregnated between said polarizable electrodes.

#### Detailed Description of the Invention

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The present invention is hereinafter described in detail.

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The active carbon used in the present invention is not particularly restricted with respect to the type and includes those obtained by carbonizing a natural fiber (e.g. sawdust or coconut husk), an aromatic polycyclic compound present in coal, petroleum or the like, or a synthetic resin of phenolic resin type, acrylic resin type, aromatic polyamide type, cellulose type or the like and then activating the resulting material by an ordinary method. The form of the active carbon may be any of a powder, granules, a fiber, etc. The specific surface area of the active carbon has no particular restriction, either but is preferably 500 m<sup>2</sup>/g or more.

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The thermosetting resin used in the present invention is not particularly restricted with respect to its composition and includes known resins such as polycarbodiimide resin, phenolic resin, furan resin, epoxy resin and the like.

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The fiber capable of vaporizing upon heating, used in the present invention is not particularly restricted and can be any synthetic or natural fiber capable of vaporizing at the heat-treating temperature or pyrolyzing temperature adopted in the process (described later) for producing a polarizable electrode for electric double-layer capacitor according to the present invention. The fiber can be exemplified by a polyvinyl alcohol, a polyethylene, a polystyrene, a polypropylene, a polyester, a polyethylene glycol and a cellulose (these are hereinafter abbreviated to "fiber component").

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In producing the polarizable electrode of the present invention for electric double-layer capacitor, there is first prepared an active carbon mixture by mixing an active carbon, a thermosetting resin and a fiber component all mentioned above. In this mixing step, there can be used a known method ordinarily used in the mixing of such components, for example, a stirring rod, a kneader, a ball mill, a mixer, a static mixer and a ribbon mixer.

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The proportions of the active carbon and the fiber component can be determined depending upon, for example, the intended properties of the polarizable electrode to be produced. For example, the proportion of the active carbon is 100 parts by weight and the proportion of the fiber component is 0.01-100 parts by weight, preferably 0.05-80 parts by weight. When the proportion of the fiber component is less than the range, it may happen that the discontinuous portions of electrode free from any solid active carbon are blocked owing to the shrinkage of electrode during the pyrolyzing step described later and, as a result, the electrode is not well impregnated with an electrolyte and has a high internal resistance. Conversely when the proportion of the fiber component is more than the range, it may happen that the electrode has a low strength and is unable to withstand the actual use.

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The proportions of the active carbon and the thermosetting resin can also be determined depending upon, for example, the intended properties of the polarizable electrode to be produced. For example, the proportion of the active carbon is 100 parts by weight and the proportion of the thermosetting resin is 0.5-100 parts by weight, preferably 1-50 parts by weight.

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Depending upon the case, there may be used, in addition to the above components, an electrically conductive agent such as expanded graphite, graphite, carbon black, ketjen black, carbon whiskers, metal powder and the like.

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The above-prepared active carbon mixture is then molded, as necessary, into a desired shape. This molding step can be conducted by a conventionally known method such as pressure molding, hydrostatic molding, extrusion molding, injection molding, belt pressing, roll pressing or the like. Incidentally, this molding step can be omitted depending upon the shape of the active carbon mixture.

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The molded active carbon mixture is heat-treated to vaporize the fiber component present therein. The atmosphere used in this step may be a conventionally known gas, for example, at least one gas selected from non-oxidizing gases such as vacuum, argon, hydrogen and the like, or from oxidizing gases such as air, carbon dioxide, oxygen, propane gas and the like. The heat-treatment temperature used in this step can be determined depending upon, for example, the thermal decomposabilities of the fiber component, active carbon and thermosetting resin present in the active carbon mixture, but is, for example, 100-600 °C, preferably 150-550 °C.

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The heat-treatment step may be omitted because it is conducted to vaporize the fiber component beforehand to shorten the time of the pyrolyzing step described later.

The material obtained by the heat-treatment step is then pyrolyzed. This pyrolyzing step can be conducted by any conventionally known method in, for example, a non-oxidizing atmosphere such as

vacuum, argon, hydrogen or the like. The pyrolyzing temperature has no upper limit but the pyrolyzing is conducted for example, at 600-3,000 °C, preferably at 700-1,500 °C. Pyrolyzing at temperatures higher than 3,000 °C invites severe oxidation and wastage of kiln and is not realistic. Pyrolyzing at temperatures lower than 600 °C gives an electrode of high internal resistance and of small capacity.

5 The material obtained by the pyrolyzing step is cut into a desired shape to obtain a polarizable electrode for electric double-layer capacitor. The cutting can be made by any conventionally known method such as cutting by cutter, cutting by ultrasonic wave, or the like.

The cutting may be conducted not after the pyrolyzing step but after or before the heat-treatment step, or may be omitted depending upon the shape of the active carbon mixture.

10 The thus-obtained polarizable electrode for electric double-layer capacitor according to the present invention comprises a solid active carbon obtained by pyrolyzing a mixture mainly containing an active carbon and a thermosetting resin and has, on the surface and/or inside, discontinuous portions free from said solid active carbon. Herein, the discontinuous portions refer to holes, gaps, dents, grooves, etc. and are formed by the vaporization of the fiber component, or by the deformation or compression of the holes, etc. 15 formed as above, occurring as a result of the shrinkage of the active carbon mixture during its heat-treatment or pyrolyzing.

In the present invention, there is used a fiber component as the component capable of vaporizing upon heating, and the fiber component has a high aspect ratio and tends to align in one direction owing to the pressure applied during molding. Therefore, when the active carbon mixture is heat-treated to vaporize the 20 fiber component and the resulting material is pyrolyzed in an inert gas, the resulting polarizable electrode has discontinuous portions (e.g. throughholes) having a shape corresponding to the shape of the fiber component.

Depending upon the direction of the cutting conducted after heat treatment or pyrolyzing, the 25 polarizable electrode can have holes each having a direction parallel or nearly parallel, or perpendicular or nearly perpendicular to the electrode surface and thereby can easily be impregnated with an electrolyte.

When the discontinuous portions are holes, the small holes having diameters of 1 nm to 5 mm are 95% or more of the total holes present in the polarizable electrode for electric double-layer capacitor according to the present invention. The porosity (the proportion of volume of total holes) in the present polarizable electrode for electric double-layer capacitor is 20-80%.

30 By using at least a pair of the thus-obtained polarizable electrode for electric double-layer capacitor as a positive electrode and a negative electrode, and appropriate electrolyte impregnated between these electrodes, an electric double-layer capacitor having a low internal resistance according to the present invention can be produced. Preferably, these electrodes are firmly bonded to an appropriate collector electrode.

35 As the electrolyte, for example, an organic electrolyte obtained by dissolving an electrolyte such as LiAsF<sub>6</sub>, LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiClO<sub>4</sub>, tetraalkylammonium, tetrafluoroborate in a solvent such as ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, γ-butyrolactone, acetonitrile, 1,2-dimethoxyethane, sulfolane, nitromethane or a mixture thereof, and an aqueous electrolyte obtained by dissolving an electrolyte such as KOH, NaOH, H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>, ZnCl, ZnBr<sub>2</sub> in water, can be used.

40 The present invention is hereinafter described specifically by way of Examples.

#### Example 1

There were mixed a polycarbodiimide resin powder (average particle diameter = 10 μm), an active carbon powder (average particle diameter = 10 μm, specific surface area = 1,800 m<sup>2</sup>/g) and a PVA (polyvinyl alcohol) short fiber (fiber diameter = 20 μm, fiber length = 3 mm). The mixing ratio of the three components is shown in Table 1. In Table 1, each number is by parts by weight (this applies also to Tables 3, 5, 8, 12 and 15).

Table 1

No.	Active carbon	Thermosetting resin	PVA short fiber
1-1	100	0.5	0.01
1-2	100	0.5	100
1-3	100	100	0.01
1-4	100	100	100

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Each of the above mixtures was stirred in a ball mill for 24 hours. The resulting material was placed in a square mold of 50 mm x 50 mm (internal dimension) and subjected to pressure molding at a pressure of 30 kg/cm<sup>2</sup> at 100 °C for 30 minutes. The molded article was heat-treated up to 400 °C in the air to vaporize the fiber and then pyrolyzed up to 900 °C in a nitrogen gas atmosphere. The pyrolyzing product was cut so that the throughholes were perpendicular to the product (electrode) surface, to prepare sheet electrodes (polarizable electrodes) each of 3 mm in thickness. Each electrode was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by a mercury porosimetry. A collector electrode (a vitreous carbon produced by Nissinbo Industries, Inc. was used as the collector) was bonded to the polarizable electrode by the use of a conductive adhesive. Two same such laminates were used as a positive electrode and a negative electrode and were vacuum-impregnated with a propylene carbonate solution containing 1 mole/liter of tetrabutylammonium perchlorate, whereby electric double-layer capacitors were produced. A constant current of 1 kHz and 10 mA was passed through each capacitor and the voltage between the electrodes was measured to determine the equivalent series resistance of the capacitor. The porosity, the proportion of small holes of 1 nm to 5 mm in diameter in total holes and the equivalent series resistance are shown in Table 2.

Table 2

No.	Equivalent series resistance (Ω)	Porosity (%)	Proportion of small holes (1 nm to 5 mm in dia.) in total holes (%)
1-1	4.00	40	95
1-2	1.00	80	98
1-3	2.00	20	95
1-4	0.50	70	96

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## Example 2

There were mixed a phenolic resin powder (average particle diameter = 10 μm), an active carbon powder (average particle diameter = 10 μm, specific surface area = 1,800 m<sup>2</sup>/g) and a PVA short fiber (fiber diameter = 20 μm, fiber length = 3 mm). The mixing ratio of the three components are shown in Table 3.

Table 3

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No.	Active carbon	Thermosetting resin	PVA short fiber
2-1	100	0.5	0.01
2-2	10	0.5	100
2-3	100	100	0.01
2-4	100	100	100

Each of the above mixtures was stirred, molded and heat-treated in the same manner as in Example 1. The pyrolyzing product was cut so that the throughholes were parallel to the product (electrode) surface, to prepare sheet electrodes (polarizable electrodes) each of 3 mm in thickness. Each electrode was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by a mercury porosimetry. A collector electrode (a vitreous carbon produced by Nisshinbo Industries, Inc. was used as the collector) was bonded to the polarizable electrode by the use of a conductive adhesive. Using two same such laminates as a positive electrode and a negative electrode, electric double-layer capacitors were produced, and the equivalent series resistance of the capacitor was determined in the same manner as in Example 1. The porosity, the proportion of small holes of 1 nm to 5 mm in diameter in total holes and the equivalent series resistance are shown in Table 4.

Table 4

No.	Equivalent series resistance ( $\Omega$ )	Porosity (%)	Proportion of small holes (1 nm to 5 mm in dia.) in total holes (%)
2-1	4.20	43	96
2-2	1.06	80	99
2-3	2.12	20	95
2-4	0.53	72	96

## Example 3

There were mixed a polycarbodiimide resin powder (average particle diameter = 10  $\mu\text{m}$ ), an active carbon powder (average particle diameter = 10  $\mu\text{m}$ , specific surface area = 1,800  $\text{m}^2/\text{g}$ ), a PVA short fiber (fiber diameter = 20  $\mu\text{m}$ , fiber length = 3 mm) and an expanded graphite powder (average particle diameter = 10  $\mu\text{m}$ ). The mixing ratio of the four components is shown in Table 5.

Table 5

No.	Active carbon	Polycarbodiimide resin	Expanded graphite	PVA short fiber
3-1	100	0.5	0.01	0.01
3-2	100	0.5	0.01	100
3-3	100	0.5	1000	0.01
3-4	100	0.5	1000	100
3-5	100	100	0.01	0.01
3-6	100	100	0.01	100
3-7	100	100	1000	0.01
3-8	100	100	1000	100

Each of the above mixtures was stirred, molded and heat-treated in the same manner as in Example 1. The pyrolyzing product was cut so that the throughholes were perpendicular to the product (electrode) surface, to prepare sheet electrodes (polarizable electrodes) each of 3 mm in thickness. Each electrode was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by a mercury porosimetry. A collector electrode (a vitreous carbon produced by Nisshinbo Industries, Inc. was used as the collector) was bonded to the polarizable electrode by the use of a conductive adhesive. Using two same such laminates as a positive electrode and a negative electrode, electric double-layer capacitors were produced, and the equivalent series resistance of the capacitor was determined in the same manner as in Example 1. The porosity, the proportion of small holes of 1 nm to 5 mm in diameter in total holes and the equivalent series resistance are shown in Table 6.

Table 6

No.	Equivalent series resistance (mΩ)	Porosity (%)	Proportion of small holes (1 nm to 5 mm in dia.) in total holes (%)
3-1	3000	41	95
3-2	750	79	98
3-3	100	22	95
3-4	25	75	96
3-5	2700	31	95
3-6	960	80	99
3-7	30	20	95
3-8	7	70	96

## 20 Example 4

Using each of the polarizable electrodes prepared in Example 1, a positive electrode and a negative electrode were prepared. They were vacuum-impregnated with an aqueous solution containing 30% by weight of sulfuric acid, whereby electric double-layer capacitors were produced. Each capacitor was determined for equivalent series resistance in the same manner as in Example 1. The results are shown in Table 7. Each capacitor was charged with and discharged a current of 200 A and then was observed. The observation results are shown in Table 18.

Table 7

No.	Equivalent series resistance (mΩ)
4-1	65
4-2	15
4-3	31
4-4	8

## 40 Example 5

There were mixed a phenolic resin powder (average particle diameter = 10 μm), an active carbon powder (average particle diameter = 10 μm, specific surface area = 1,800 m<sup>2</sup>/g) and a PVA (polyvinyl alcohol) short fiber (fiber diameter = 20 μm, fiber length = 3 mm). The mixing ratio of the three components is shown in Table 8.

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Table 8

No.	Active carbon	Polycarbodiimide resin	PVA short fiber
5-1	100	0.5	0.01
5-2	100	0.5	100
5-3	100	100	0.01
5-4	100	100	100

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Each of the above mixtures was stirred, molded and heat-treated in the same manner as in Example 1. The pyrolyzing product was cut so that the throughholes were perpendicular to the product (electrode) surface, to prepare sheet electrodes (polarizable electrodes) each of 3 mm in thickness. Each electrode was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by a mercury porosimetry. A collector electrode (a vitreous carbon produced by Nissinbo Industries, Inc. was used as the collector) was bonded to the polarizable electrode by the use of a conductive adhesive in the same manner as in Example 1. Using two same such laminates as a positive electrode and a negative electrode, electric double-layer capacitors were produced and the equivalent series resistance of each capacitor was determined in the same manner as in Example 1. The porosity, the proportion of small holes of 1 nm to 5 mm in diameter in total holes and the equivalent series resistance are shown in Table 9.

Table 9

No.	Equivalent series resistance ( $\Omega$ )	Porosity (%)	Proportion of small holes (1 nm to 5 mm in dia.) in total holes (%)
5-1	6.00	40	95
5-2	1.20	80	98
5-3	2.70	20	95
5-4	0.70	70	96

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## Example 6

Using sheet electrode produced in Example 1 and corresponds to the electric double-layer capacitor No. 1-2, there were produced electric double-layer capacitor in the same manner as Example 1. The capacitor was measured for equivalent series resistances after 1, 100, 500 and 1,000 cycles in the same manner as in Example 1. The results are shown in Table 10.

Table 10

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	Cycles (times)			
	1	100	500	1000
Equivalent series resistance ( $\Omega$ )	1.00	1.01	1.01	1.02

## Example 7

Using sheet electrode produced in Example 1 and corresponds to the electric double-layer capacitor No. 1-2, there were produced three electric double-layer capacitors in the same manner as in Example 1. Each capacitor was measured for equivalent series resistance in the same manner as in Example 1. The results are shown in Table 11.

Table 11

	Electrode thickness (mm)			
	1	3	5	
5	Equivalent series resistance ( $\Omega$ )	0.8	1.0	1.2

## 10 Comparative Example 1

There were mixed a polycarbodiimide resin powder (average particle diameter = 10  $\mu\text{m}$ ) and an active carbon powder (average particle diameter = 10  $\mu\text{m}$ , specific surface area = 1,800  $\text{m}^2/\text{g}$ ). The mixing ratios of the two components are shown in Table 12.

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Table 12

No.	Active carbon	Polycarbodiimide resin
20	Comp. Ex. 1-1	100
	Comp. Ex. 1-2	100

- Each of the above mixtures was stirred, molded and heat-treated in the same manner as in Example 1.  
 25 From each pyrolyzing product was prepared a sheet electrode (polarizable electrode) of 3 mm in thickness. Each polarizable electrode was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by the mercury porosimetry. A collector electrode (a vitreous carbon produced by Nissinbo Industries, Inc. was used as the collector) was bonded to the polarizable electrode by the use of a conductive adhesive in the same manner as Example 1. Using two same such laminates as a positive  
 30 electrode and a negative electrode, electric double-layer capacitors were produced, and each capacitor was determined for equivalent series resistance in the same manner as in Example 1. The porosity, the proportion of small holes of 1 nm to 5 mm in diameter in total holes and the equivalent series resistance are shown in Table 13.

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Table 13

No.	Equivalent series resistance ( $\Omega$ )	Porosity (%)	Proportion of small holes (1 nm to 5 mm in dia.) in total holes (%)
40	Comp. Ex. 1-1	70	85
	Comp. Ex. 1-2	37	10

## 45 Comparative Example 2

- Using sheet electrode produced in Example 1 and corresponds to the electric double-layer capacitor No. 1-1, there were produced three electric double-layer capacitors in the same manner as in Example 1. Each capacitor was measured for equivalent series resistance in the same manner as in Example 1. The  
 50 results are shown in Table 14.

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Table 14

	Electrode thickness (mm)			
	1	3	5	
5	Equivalent series resistance ( $\Omega$ )	50	70	280

## 10 Comparative Example 3

There were mixed a phenolic resin powder (average particle diameter = 10  $\mu\text{m}$ ) and an active carbon powder (average particle diameter = 10  $\mu\text{m}$ , specific surface area = 1,800  $\text{m}^2/\text{g}$ ). The mixing ratio of the above two components is shown in Table 15.

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Table 15

No.	Active carbon	Phenolic resin
20	Comp. Ex. 3-1	100
	Comp. Ex. 3-2	100

Each of the above mixtures was stirred, molded and heat-treated in the same manner as in Example 1. From each pyrolyzing product was prepared a sheet electrode (polarizable electrode) of 3 mm in thickness. Each polarizable electrode was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by the mercury porosimetry. A collector electrode (a vitreous carbon produced by Nissinbo Industries, Inc. was used as the collector) was bonded to the polarizable electrode by the use of a conductive adhesive. Using two same such laminates as a positive electrode and a negative electrode, electric double-layer capacitors were produced in the same manner as in Example 1. A constant current of 1 kHz and 10 mA was passed through each capacitor and the voltage between the electrodes was measured to determine the equivalent series resistance of the capacitor. The porosity, the proportion of small holes of 1 nm to 5 mm in diameter in total holes and the equivalent series resistance are shown in Table 16.

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Table 16

No.	Equivalent series resistance ( $\Omega$ )	Porosity (%)	Proportion of small holes (1 nm to 5 mm in dia.) in total holes (%)
40	Comp. Ex. 3-1	100	84
	Comp. Ex. 3-2	47	9

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## Comparative Example 4

Using each of the polarizable electrodes prepared in Comparative Example 3, a positive electrode and a negative electrode were prepared. They were vacuum-impregnated with an aqueous solution containing 30% by weight of sulfuric acid, whereby electric double-layer capacitors were produced. Each capacitor was determined for equivalent series resistance in the same manner as in Example 1. The results are shown in Table 17. Each capacitor was charged with and discharged a current of 200 A and then was observed. The observation results are shown in Table 18.

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Table 17

No.	Equivalent series resistance ( $\text{m}\Omega$ )
Comp. Ex. 4-1	30
Comp. Ex. 4-2	12

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Table 18

No.	Appearance of electrodes
4-1	Normal
4-2	Normal
4-3	Normal
4-4	Normal
Comp. Ex. 4-1	Electrodes collapsed into pieces.
Comp. Ex. 4-2	Electrodes collapsed into pieces.

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## Comparative Example 5

A phenolic foam having a bulk density of 0.1 g/cm<sup>3</sup> and a foam direction perpendicular to the surface of the electrode to be prepared therefrom, was pyrolyzed at 900°C in a nitrogen gas atmosphere. The 30 pyrolyzing product was kept for 3 hours in a mixture of nitrogen gas and carbon dioxide gas for activation. The activation product was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by the mercury porosimetry, which were 15% and 93%, respectively. The activation product was cut into a size of 10 mm (diameter) x 3 mm (thickness) and bonded to a vitreous carbon (a product of Nissinbo Industries, Inc.) by the use of a conductive adhesive. The resulting laminate was 35 vacuum-impregnated with a propylene carbonate solution containing 1 mole/liter of tetrabutylammonium perchlorate, whereby an electric double-layer capacitor was produced. The capacitor was determined for equivalent series resistances after 1, 100, 500 and 1,000 cycles in the same manner as in Example 1. The results are shown in Table 19.

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Table 19

	Cycles (times)			
	1	100	500	1000
Equivalent series resistance ( $\Omega$ )	21	50	153	221

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## Comparative Example 6

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To each of the two polarizable electrodes prepared in Comparative Example 1, a hole of a size of 8 mm in diameter was made with a drill to prepare two polarizable electrodes. Each electrode was measured for porosity and proportion of small holes of 1 nm to 5 mm in diameter in total holes, by the mercury porosimetry. Each electrode was bonded to a collector electrode (a vitreous carbon produced by Nissinbo Industries, Inc. was used as the collector) by the use of a conductive adhesive, in the same manner as in Example 1. Using two same such laminates as a positive electrode and a negative electrode, two electric double-layer capacitors were produced in the same manner as in Example 1. The capacitors were measured for electrostatic capacity. The capacitors were determined for equivalent series resistance in the 55

same manner as in Example 1. The porosity, the proportion of small holes of 1 nm to 5 mm in diameter in total holes, and the equivalent series resistance are shown in Table 20.

Table 20

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No.	Equivalent series resistance ( $\Omega$ )	Porosity (%)	Proportion of small holes (1 nm to 5 mm in dia.) in total holes (%)
Comp. Ex. 6-1	200	85	90
Comp. Ex. 6-2	500	87	10

As is clear from the above, the electric double-layer capacitor of the present invention has a sufficiently low internal resistance and yet a long cycle life.

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### Claims

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1. A polarizable electrode for electric double-layer capacitor, which comprises a solid active carbon obtained by pyrolyzing a mixture mainly containing an active carbon and a thermosetting resin and which has, on the surface and/or inside, discontinuous portions free from said solid active carbon.

2. A polarizable electrode for electric double-layer capacitor according to Claim 1, wherein the solid active carbon is obtained by pyrolyzing a mixture mainly containing an active carbon and a thermosetting resin, in a non-oxidizing atmosphere.

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3. A polarizable electrode for electric double-layer capacitor according to Claim 1, wherein the discontinuous portions free from the solid active carbon are holes.

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4. A polarizable electrode for electric double-layer capacitor according to Claim 3, wherein the discontinuous portions free from the solid active carbon are holes whose directions are parallel or nearly parallel to the surface of the electrode.

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5. A polarizable electrode for electric double-layer capacitor according to Claim 3, wherein the discontinuous portions free from the solid active carbon are holes whose directions are perpendicular or nearly perpendicular to the surface of the electrode.

6. A polarizable electrode for electric double-layer capacitor according to Claim 3, wherein the small holes having diameters of 1 nm to 5 mm occupy 95% or more of the total holes as discontinuous portions free from the solid active carbon.

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7. A polarizable electrode for electric double-layer capacitor according to Claim 3, wherein the porosity given by holes as discontinuous portions free from the solid active carbon is 20-80%.

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8. A polarizable electrode for electric double-layer capacitor according to Claim 3, wherein the discontinuous portions free from the solid active carbon are throughholes.

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9. A polarizable electrode for electric double-layer capacitor according to Claim 1, wherein the discontinuous portions free from the solid active carbon are formed by adding, to a mixture mainly containing an active carbon and a thermosetting resin, a fiber capable of vaporizing upon heating and then heating the resulting mixture.

10. A polarizable electrode for electric double-layer capacitor according to Claim 9, wherein the fiber capable of vaporizing upon heating is a synthetic fiber or a natural fiber.

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11. A polarizable electrode for electric double-layer capacitor according to Claim 10, wherein the fiber capable of vaporizing upon heating is a polyvinyl alcohol, a polyethylene, a polystyrene, a polypropylene, a polyester, a polyethylene glycol or a cellulose.

12. A process for producing a polarizable electrode for electric double-layer capacitor, which comprises pyrolyzing a mixture mainly containing an active carbon, a thermosetting resin and a fiber capable of vaporizing upon heating, to vaporize said fiber.
- 5    13. A process for producing a polarizable electrode for electric double-layer capacitor, which comprises heat-treating a mixture mainly containing an active carbon, a thermosetting resin and a fiber capable of vaporizing upon heating, to vaporize said fiber and then pyrolyzing the resulting material.
- 10    14. A process for producing a polarizable electrode for electric double-layer capacitor according to Claim 12 or 13, wherein the fiber capable of vaporizing upon heating is a synthetic fiber or a natural fiber.
- 15    15. A process for producing a polarizable electrode for electric double-layer capacitor according to Claim 14, wherein the fiber capable of vaporizing upon heating is a polyvinyl alcohol, a polyethylene, a polystyrene, a polypropylene, a polyester, a polyethylene glycol or a cellulose.
16. A process for producing a polarizable electrode for electric double-layer capacitor according to Claim 12 or 13, which comprises a step of molding into a desired shape the mixture mainly containing an active carbon, a thermosetting resin and a fiber capable of vaporizing upon heating.
- 20    17. A process for producing a polarizable electrode for electric double-layer capacitor according to Claim 12 or 13, which comprises a step of cutting into a desired shape.
18. An electric double-layer capacitor which comprises at least a pair of polarizable electrode according to any of Claims 1- 11 and an electrolyte impregnated there-between.
- 25    19. An electric double-layer capacitor according to Claim 18, whrerein each polarizable electrode is firmly bonded to a collector electrode respectively.
20. A shaped material used for production of a polarizable electrode for electric double-layer capacitor, which is obtained by heat-treating a mixture mainly containing an active carbon, a thermosetting resin and a fiber capable of vaporizing upon heating, to vaporize the fiber.
- 30    21. A shaped material used for production of a polarizable electrode for electric double-layer capacitor, which is obtained by pyrolyzing a mixture mainly containing an active carbon, a thermosetting resin and a fiber capable of vaporizing upon heating, to vaporize the fiber.

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European Patent  
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## EUROPEAN SEARCH REPORT

Application Number  
EP 94 11 8313

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	<p>EXTENDED ABSTRACTS FALL MEETING (1993), no. 2, 10 October 1993 - 15 October 1993 NEW ORLEANS, NJ, US, page 130 XP 000422306</p> <p>YUKARI KIBI ET AL. 'charge-discharge characteristics of activated carbon/carbon composite electrodes for electric double layer capacitor'            * paragraph 1 - paragraph 2 *            * paragraph 4 *</p> <p>---</p>	1-3,9, 10,12, 14,16-21	H01G9/058 H01G9/00
A		6,7,13	
A	<p>IEEE TRANSACTIONS ON COMPONENTS, HYBRIDS AND MANUFACTURING TECHNOLOGY, vol. 16, June 1993 NEW YORK, US, pages 431-436, XP 000400460</p> <p>JUNJI TABUCHI ET AL. 'Large Capacitance Electric Double Layer Capacitor Using Activated Carbon/Carbon Composite'</p> <p>-----</p>		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6) H01G
<p>The present search report has been drawn up for all claims</p>			
Place of search  THE HAGUE	Date of completion of the search  18 April 1995	Examiner  Goossens, A	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			